

Kinetics, Mechanism and Product Yields in the Atmospheric Oxidation of Dimethylsulfide

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LONG-TERM GOALS

Dimethylsulfide (DMS, CH_3SCH_3) produced by phytoplankton emission is thought to be the major source of the sulfate and methanesulfonate aerosol found in the marine boundary layer. An understanding of the mechanism of formation of these aerosols is critical to understanding the factors which control visibility in the marine boundary layer. The primary objective of this research effort is the determination of the detailed mechanism of, and final products yields from, the OH initiated gas phase oxidation of dimethylsulfide (DMS).

OBJECTIVES

Our objectives include the determination of a) the effective rate coefficients for the OH initiated oxidation of DMS under atmospheric conditions, b) the elementary rates for adduct formation, decomposition and reaction, b) direct confirmation of production, and quantitative product yields of potential reaction products and intermediates such sulfur dioxide (SO_2) and dimethyl sulfoxide (DMSO: $(\text{CH}_3)_2\text{SO}$).

APPROACH

Our studies utilize the Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence (PLP-PLIF) technique. Laser photolysis of a suitable precursor, either H_2O_2 or HNO_3 , is used to generate OH. The rate of loss of OH, and the appearance of potential products such as SO_2 , SO and CH_3S are monitored by a second "probe" laser using laser induced fluorescence. Kinetic information is obtained by varying the delay between the photolysis and probe lasers, mapping out a temporal profile of the species of interest.

WORK COMPLETED

Our current proposal identified discrepancies in the experimental data base on DMS chemistry and led us to conclude that there was a significant possibility that the currently recommended rate coefficient for the reaction of OH with DMS under atmospheric conditions is too slow. An accurate value of this rate coefficient is critical in defining the lifetime of DMS in the marine boundary layer and hence the

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rate at which it is oxidized to products, some of which may act as condensation nuclei. We have completed an extensive series of experiments measuring the effective rate coefficient for the reaction of OH with DMS and DMS-d6 as a function of O₂ partial pressure, at 600 Torr total pressure (O₂ + N₂) at 296, 261 and 240 K. In addition we have measured the forward equilibration rate coefficient for OH with both DMS and DMS-d6 as a function of pressure in N₂. A paper describing the O₂ dependence is near completion and will be submitted to Geophysical Research Letters shortly.

RESULTS

At the low NO_x levels that are characteristic of the remote marine boundary layer, reaction with OH is the initial step in DMS oxidation.

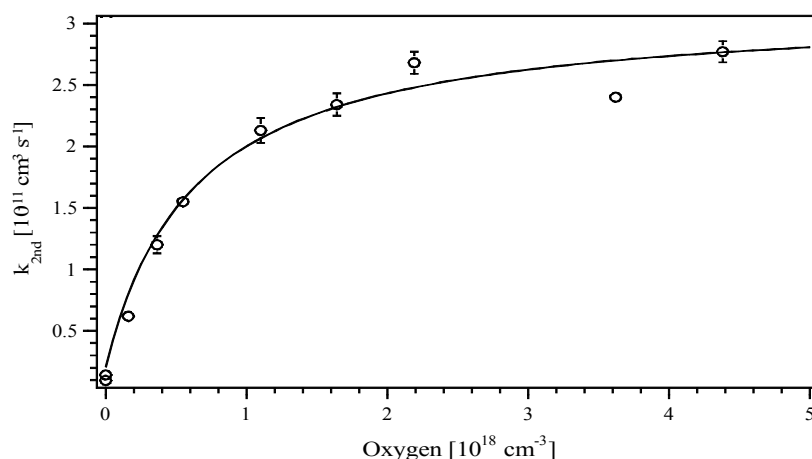


The OH initiated oxidation of DMS proceeds via a complex mechanism which can be described by the reaction sequence (written here for DMS-d6):



Because of this complex mechanism the effective rate coefficients for reactions (1) and (2) depend on the partial pressure of O₂ at any total pressure. Figure 1 shows our results for the variation

Dependence of total reaction rate on oxygen partial pressure
at 600 Torr total pressure and 240 K

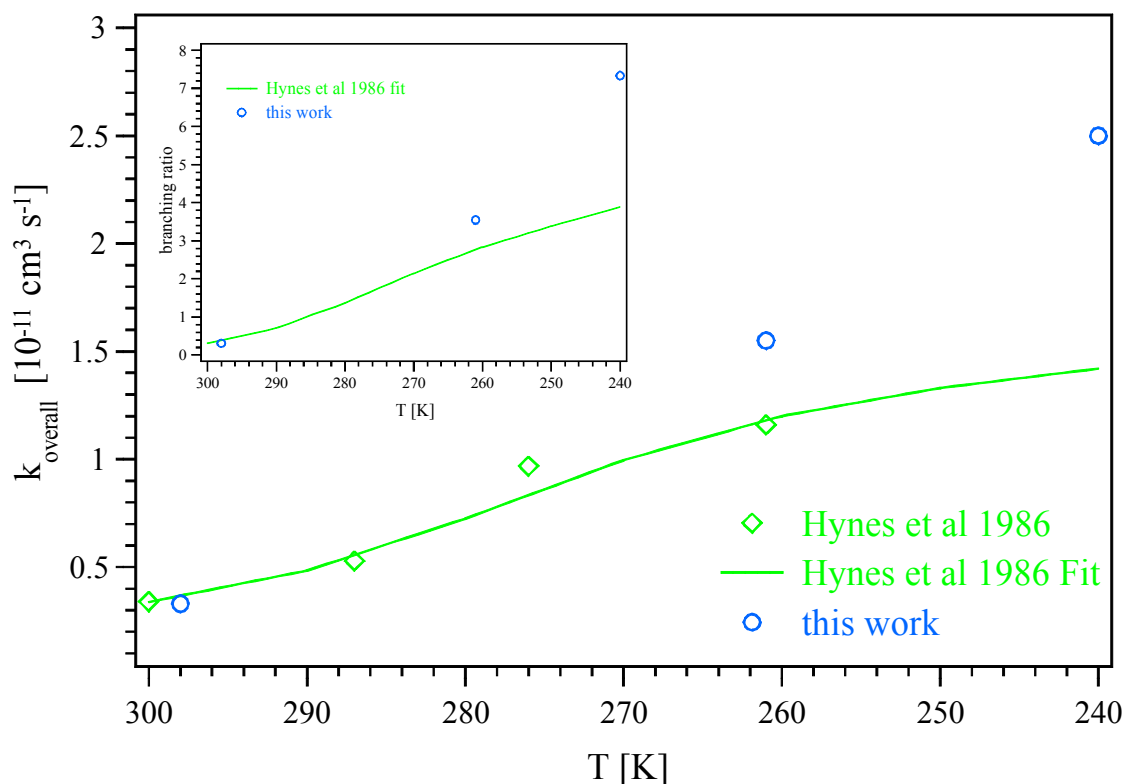


in the effective rate of reaction (2) at 600 Torr total pressure at 240 K. The currently recommended rates for atmospheric modeling of DMS oxidation are based on the 1986 work of Hynes et al. They found that the effective rate coefficient for reaction (1) and its deuterated analog, reaction (2), was dependent on oxygen concentration and proposed the mechanism shown above. They determined the temperature dependence of the effective rate for reaction (1) in 760 Torr of air, together with the

temperature dependence of the branching ratio. The results were well described by a value for the forward addition rate coefficient, k_{2b} , of $1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature. The two channel mechanism has been widely accepted as the operative mechanism for the OH initiated oxidation of DMS, and the directly determined rates and inferred branching ratio's recommended as the best currently available for atmospheric modeling purposes. Our new results are compared with the 1986 data in Figure 2 which shows the temperature dependence of the O_2 enhancement in the effective rate coefficient for reactions (1) and (2) in one atmosphere of air using the 1986 expression of Hynes et al.

For comparison the plot includes the points obtained in 600 Torr of air at 261 and 240 K in this work. The inset in Figure 2 shows the temperature dependence of the branching ratio between the addition and abstraction channel for reaction (1) in 760 Torr of air based on the 1986 work. Again, for comparison we include the branching ratio measured in this work at 600 Torr and 240 K together the value obtained at 261 K assuming the O_2 enhancement in reactions (1) and (2) is the same. We would expect

k_{overall} and branching ratios between 240 and 300 K



the 760 Torr values to be a little higher than the 600 Torr values reported here, nevertheless this work clearly shows that the 1986 expression underestimates both the effective rate coefficient for reaction (1) at low temperatures together with the branching ratio between addition and abstraction. The 1986

expression, an empirical fit to the observed O₂ enhancements in reactions 1 and 2 is heavily weighted by the single 261 K point predicting a relatively small temperature dependence in the O₂ enhancement below and producing a low value for k_{2b}.

IMPACT

These results show that 1986 expression of Hynes et al. for the effective rate of the OH initiated oxidation of DMS significantly underestimates both the effective rate and branching ratio between abstraction and addition at low temperatures. Current models of the high latitude oxidation of DMS should be significantly impacted by these results.

TRANSITIONS

The potential implications of this work for particle formation in the marine boundary layer will require a completion of the laboratory work and modeling studies.

RELATED PROJECTS

In our NSF sponsored work on HO_x cycling we have shown that the quantum yield for O¹D formation from ozone photolysis has a significant long wavelength component, part of which is spin forbidden. Our work shows that spin forbidden photolysis of ozone in the Huggins bands occurs out to at least 375 nm. This implies that current models underestimate OH concentrations, particularly at low temperatures and high zenith angles. Since OH is a primary oxidant for both DMS and SO₂ these results will feedback into models of marine boundary layer chemistry and imply higher oxidation rates of both DMS and SO₂. In related ONR sponsored work we are attempting to develop novel laser based instrumentation to allow near real-time sodium measurements on individual, size-segregated marine aerosols.

REFERENCES

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